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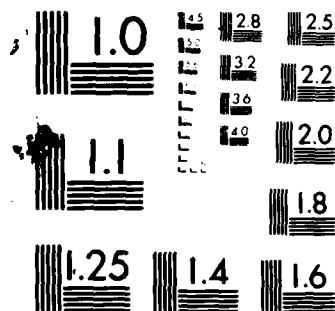
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Energy transfer, rotational relaxation, laser, hydrogen fluoride, deuterium fluoride, vibrational relaxation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Combining the techniques of direct excitation of overtone vibrations and time resolved spectroscopic detection permits detailed measurements of the vibrational and rotational relaxation of highly vibrationally excited molecules. Using this technique, we have measured vibrational and rotational relaxation in HF($v = 3,4,5$) between 300 K and 650 K and have compared these results to various theoretical calculations. Using laser double resonance to probe individual rotational states, we find phenomenological rotational re-
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20. laxation rate constants which decrease montonically with rotational energy change in the vibrationally excited molecule, and we have directly measured the vibrational relaxation rate constants for $v = 1$ and $v = 2$ as well as made a preliminary estimate of the (surprisingly small) fraction of the relaxation which goes by vibration-to-vibration energy transfer. With the inclusion of these mesurements, we have now determined the self-relaxation rate for HF($v = 1,2,3,4$, and 5) using laser double resonance and near-infrared fluorescence.

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COLLISIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED MOLECULES

(Contract No. N00014-79-C-0415)

1. Principal Investigator:

F. F. Crim
Assistant Professor
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

2. Contract Description:

The aspect of this work funded by the Office of Naval Research is the direct
measurement of rotational and vibrational relaxation rates of highly vibrationally
excited deuterium fluoride. We expect to uncover systematic trends related to the
initial rotational level of the excited molecule and to discover the influence
which vibrational excitation has on rotational relaxation processes.

3. Scientific Problem:

Little experimental information is available on rotational energy transfer
processes in general, and virtually none exists on the behavior of rotations in
highly vibrationally excited molecules. This study will provide some of the
first detailed data on rotational relaxation of molecules with large amounts of
vibrational energy. As discussed below, the preparation technique and final
state analysis are highly specific, so that the resulting rates represent an
average over only the thermal rotational and translational energy distribution
of the ground vibrational state collision partners. The rates come from a _direct_
(time resolved) measurement of the populations of individual rotational states.
Excitation of different vibrational states provides information on the influence
which vibrational excitation has on rotational relaxation rates, . roduces
new vibrational relaxation data, also. Our measurements will be valu.. le for
comparison to inferential techniques, such as overtone vibration linewidth measure-
ments, and as a test of promising theories based on modified forms of the sudden
approximation. These experiments on important but as yet unexplored rotational
relaxation in highly vibrationally excited molecules promise to produce unique,
detailed data which extend our fundamental and practical understanding of energy
transfer dynamics and test theoretical modesl of these processes.

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4. Scientific and Technical Approach:

The detailed measurements of this study require two essential experimental capabilities: (1) preparation of a single rotational state in highly vibrationally excited molecule and (2) temporally resolved detection of the populations of other rotational levels (as well as that of the initially excited level). We prepare the desired state by direct excitation of a molecule from its ground vibrational state to an overtone vibrational level using visible photons from a pulsed dye laser or near-infrared photons produced by stimulated Raman scattering of the dye laser pulse in hydrogen gas. Because this excitation scheme relies on small transition probabilities arising from anharmonic terms in the potential and non-linear terms in the dipole moment expansion, only a small fraction of the molecules are excited. We have demonstrated, however, that this is adequate for vibrational relaxation measurements on HF($v = 3,4,5$). [Chem. Phys. Letters 71, 258 (1980) and J. Chem. Phys. 74, 4455 (1981) and 75, 3871 (1981).] We are using a Nd:YAG/dye laser and expect that excitation of DF is quite feasible with this source. The short pulse duration ($\sim$ 6 ns) of this laser is also essential to our measurements of the temporal evoluation of individucal rotational levels. The detection scheme employs laser resonance absorption to probe a single rotational state in the highly vibrationally excited molecule. The exciting laser pulse and infrared probing radiation from a continuous HF/DF laser propagate collinearly through a long ($\sim$ 1m) cell where transient absorption of the probe radiation mirrors the temporal evolution of an individual rotational state. After the cell, the visible (preparation) beam and infrared (probe) beam are separated, and the intensity of the probe beam is recorded by a fast InAs infrared detector and transient digitizer. A multichannel ananlyzer and computer accomplish the requisite signal enhancement, and analysis of the signal amplitude and form provides relaxation rates. The exciting laser selects a single vibrational-rotational level, while the probe laser interrogates an individual state also. This excitation and detection specificity is an essential feature of the experiment which provides the detailed information desired.

Our program is directed toward developing the noted experimental capabilities through a series of necessary measurements leading to the goal of determining rotational relaxation rates in highly vibrationally excited DF. We are extending our first double resonance measurements on the $v = 2$ level of HF to rotational levels of HF($v > 2$) (which requires finding new operational limits of our infrared laser). Having achieved the HF analog of the desired measurement on DF, we will

convert our infrared laser to DF operation (a relatively straightforward task after working with high levels of HF) and perform double resonance measurements on the weaker excitation candidate DF.

5. Progress:

During the past year, we have measured the vibrational relaxation rate of HF($v = 3,4,5$) prepared by direct excitation of overtone vibrations between 300 K and 650 K in order to complement our previous room temperature work. These data test several trajectory calculations as well as other models of collisional energy transfer (G. M. Jursich and F. F. Crim, J. Chem. Phys. 74, 4455 (1981), and T. J. Foster and F. F. Crim, J. Chem. Phys. 75, 3871 (1981).) We find that vibrational relaxation is primarily by a single vibrational quantum process. These temperature dependence measurements show that the probability falls somewhat more rapidly than for $v = 1$.

We have also used our double resonance technique to determine the rotational relaxation rate in HF($v = 2$) by probing the temporal evaluation of the population of a level J for initial excitation of levels above and below it. We have monitored $J = 2-6$ populations in this way while pumping higher and lower-levels (R. A. Copeland, D. J. Pearson, and F. F. Crim, Chem. Phys. Letters 81, 541 (1981) and work in progress). We have developed computer codes for calculating the temporal evolution of the double resonance signal from the complete kinetic scheme and relaxation rate constant matrix. This code is the essential feature in fitting schemes which we use to describe our data with various scaling relationships. Our detailed data should critically test these relationships. The double resonance experiments have also yielded the vibrational relaxation rates for HF($v = 1$ and $v = 2$) and provide data for extracting the individual vibration-to-vibration and vibration-to-translation energy transfer rates in HF($v = 2$) self-relaxation.

Publications:

6. G. M. Jursich and F. F. Crim, "Vibrational Relaxation of HF($v = 3,4,5$)", J. Chem. Phys. 74, 4455 (1981).

T. J. Foster and F. F. Crim, "The Temperature Dependence of HF($v = 3,4,5$) Energy Transfer Between 300 and 650 K", J. Chem. Phys. 75, 3871 (1981).

R. A. Copeland, D. J. Pearson, and F. F. Crim, "Rotational Relaxation in HF($v = 2$)", Chem. Phys. Letters 81, 541 (1981).

7. Extenuating circumstances:

   None

8. No unspent funds will remain at the end of the contract period.

9. Two graduate students will have received their degrees during this contract period.

   D. J. Pearson (MS)

   R. A. Copeland (Ph.D.)

10. Other support:

Petroleum Research Fund	$30,000	(2 years)
Department of Energy	$103,000	(2 years)
Alfred P. Sloan Foundation	$20,000	